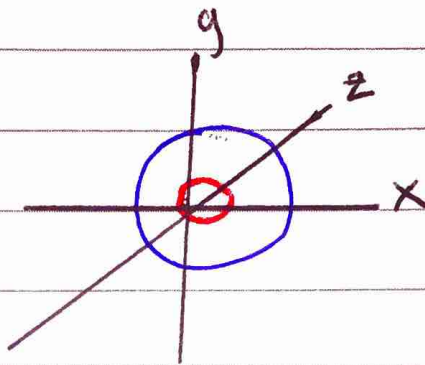
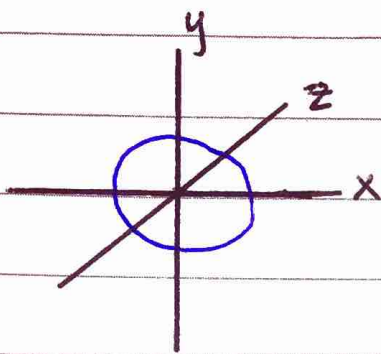
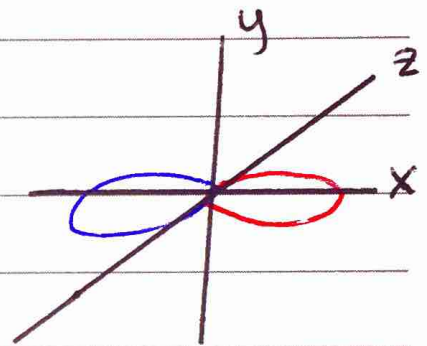
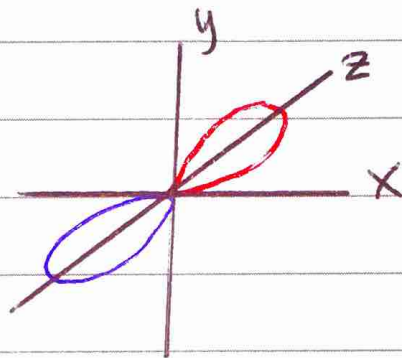
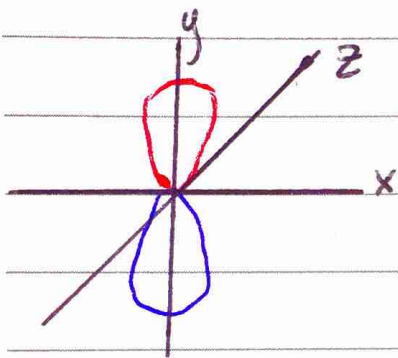


# Orbitals Review



1s orbital

2s orbital (has 1 node)



2py orbital  
(has 1 node)

2pz orbital  
(has 1 node)

2px orbital  
(has 1 node)

Degenerate orbitals (have same energy level)

\* p orbitals have two phases where electrons may exist. These lobes represent the electron density of an atom and also represent different spins

\* The node is a region of zero electron density where no electron is found

\* Electrons are lowest in energy when they occupy a 1s orbital

↳ 1s orbital is closest to the nucleus

↳ has no nodes

\* Order in which orbitals are filled follow three principles:

1) Aufbau Principle → the lowest energy orbital is filled first

2) Pauli Exclusion Principle → each orbital can have a max of 2 electrons w/ opposite spins

3) Hund's Rule → electrons are placed in each degenerate orbital first, before electrons are paired up

### \* Valence Bond Theory

• two waves approaching each other can interfere:

1) Constructively, reinforcing one another

2) Destructively, canceling each other

1



2





- The waves are an analogy for electrons:
  - a bond is the sharing of electron density between 2 atoms as a result of the constructive interference of their atomic orbitals
- $\sigma$  bond: characterized by circular symmetry with respect to the bond axis
  - ↳ all single bonds are  $\sigma$  bonds

### \* Molecular Orbitals

- Form when atoms interact and become molecules
- Forms a
  - bonding molecular orbital: lower in energy, being filled first, constructive interference
  - antibonding molecular orbital: higher in energy, destructive interference, has one node

### \* Hybridized Atomic Orbitals

#### ① $sp^3$ Hybridization

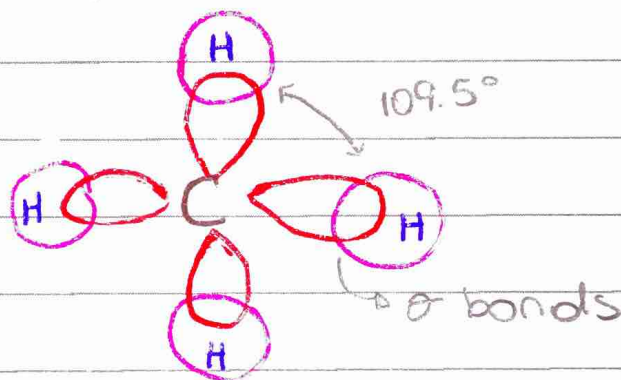
- the averaging of one s orbital and 3 p orbitals
- the 4 resulting  $sp^3$  orbitals are equal in energy
- $sp^3$  orbitals will position themselves as far away as possible due to equal energies
  - gives rise to a tetrahedral geometry

- the hybridized orbital is asymmetric
- makes the hybrid more efficient in bond formation



• Example ⇒ Methane ( $\text{CH}_4$ )

- Results from the overlap of carbon's  $sp^3$  orbitals with hydrogen's s orbital



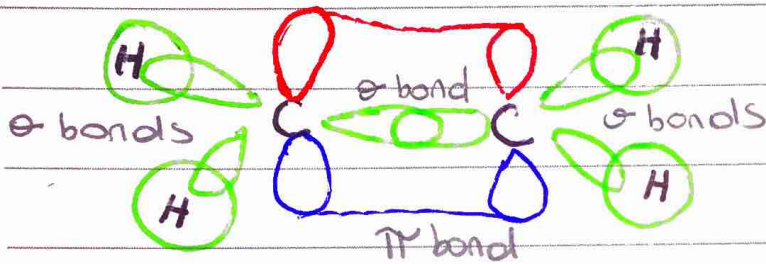
## 2) $sp^2$ Hybridization

- average between the s orbital and 2 ~~p orbitals~~ orbitals
- gives rise to a double bond
- in addition to  $\sigma$  bonds formed by the overlap of hybridized orbitals from different atoms, this hybridization creates  $\pi$  bonds:
  - the overlap of the unhybridized p orbital between two atoms
  - occurs above and below the plane of the



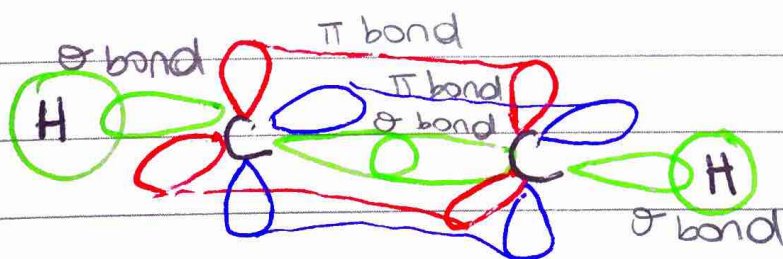
molecule (not on the bond axis)

• Example: ethylene ( $C_2H_4$ )



### 3) sp hybridization

- forms a triple bond
- average of the s orbital and 1 p orbital
  - leaves 2 p orbitals unhybridized
- sp orbitals: form  $\sigma$  bonds
- p orbitals: form  $\pi$  bonds
- Example: acetylene ( $C_2H_2$ )



### \* Steric Number + VSEPR Theory

- the total number of  $\sigma$  bonds and lone pairs of an atom
- allows for the prediction of a small molecule's geometry

- this # indicates the # of electron pairs (bonding + nonbonding) that are repelling each other

VSEPR • the repulsion causes electron pairs to arrange themselves in 3D space to be as far apart as possible

### ➡ Geometries Resulting from $sp^3$

• contain 4 pairs of electrons

- steric # 4

• must use 4 orbitals, thus being  $sp^3$

• Always tetrahedral

- If atom has all 4  $\sigma$  bonds = tetrahedral

- If has 3  $\sigma$  bonds + 1 lone pair = trigonal pyramidal (ex: ammonia  $NH_3$ )

- If has 2  $\sigma$  bonds + 2 lone pairs = bent  
(ex: water  $H_2O$ )

• lone pairs repel each other more strongly than bonds

- gives rise to smaller angles of bonds

- ex: trigonal pyramidal, bent

### ➡ Geometries resulting from $sp^2$

• contains 3 pairs of electrons

- steric # 3

• must use 3 orbitals, thus being  $sp^2$



- Always trigonal planar

• If contains 3  $\sigma$  bonds = trigonal planar geometry  
(ex:  $BH_3$ )

• If contains 2  $\sigma$  bonds + 1 lone pair = bent geometry (ex: nitrogen of an imine)

→ Geometries resulting from  $sp$

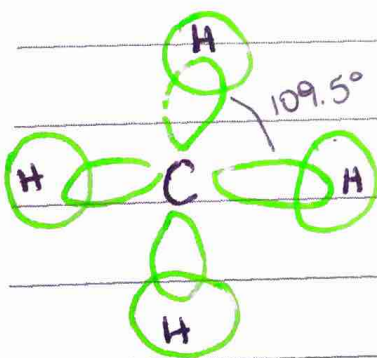
- steric # 2

- Needs 2 orbitals ( $sp$ )

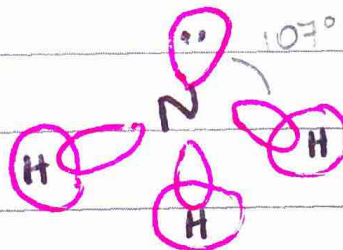
- Always linear

• Always results in two bonds and no lone pairs  
(ex:  $BeH_2$ ,  $CO_2$ )

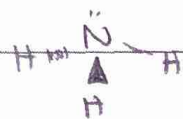
**Methane** ( $sp^3$ )



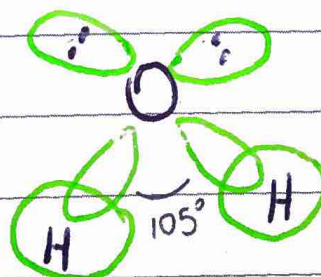
**Ammonia** ( $sp^3$ )



Trigonal  
Pyramidal



**Water** ( $sp^3$ )

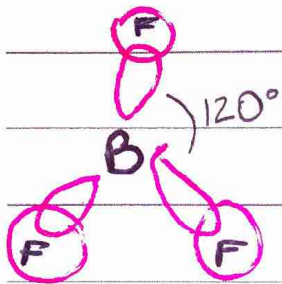


Bent



Tetrahedral

$\text{BF}_3$  ( $sp^2$ )



Trigonal Planar

Imine ( $sp^2$ )



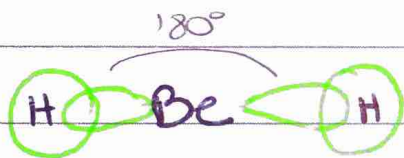
Bent

$\text{CO}_2$  ( $sp$ )



Linear

$\text{BeH}_2$  ( $sp$ )



Linear



Steric # = 4

$sp^3$

Tetrahedral arrangement of electron pairs

no lone pairs (LP)

Tetrahedral

1 LP

Trigonal Pyramidal

2 LP

Bent

Steric # = 3

$sp^2$

Trigonal Planar arrangement of electron pairs

1 LP

Bent

no LP

Trigonal Planar

Steric # = 2

$sp$

Linear arrangement of electron pairs

Linear

# Resonance

\* When an atom has an empty orbital (a  $\pm$  charge) it is  $sp^2$  hybridized and the empty orbital is a p orbital

## \* Resonance Structures

- they show that charges and electrons are spread over the molecular orbitals of the entire molecule instead of being confined to a single atom

- no single drawing adequately describes the nature of the electron density spread out over the molecule

## \* Delocalization

- the spreading of charge (+ or -)

- is a stabilizing factor for the molecule

\* Two rules to follow when drawing curved arrows for resonance structures:

1) Avoid breaking a single bond

2) Never exceed an octet for 2nd row elements

- C, N, O, F have only 4 orbitals in their valence shell

- each orbital can either form a bond or hold a lone pair

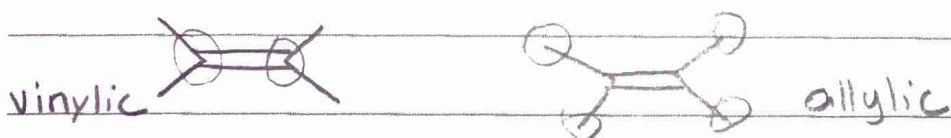


- their total number of bonds plus the # of lone pairs can never be more than 4
- only a violation if a 2nd row element exceeds an octet of electrons
  - not a violation if it has less than an octet

\* Five patterns to recognize when drawing resonance structures:

① An allylic lone pair

- in a carbon-carbon double bond, the 2 carbon atoms bearing the double bond are the vinyllic positions
- the atoms directly connected to the vinyllic positions are the allylic positions



- when you see a lone pair next to a  $\pi$  bond
- resonance structure is then obtained by drawing two curved arrows:

- one goes from the lone pair to form a  $\pi$  bond
- the other goes from the  $\pi$  bond to form a lone pair

- when the atom with the lone pair has a

negative charge, then it transfers its negative charge to the atom receiving a lone pair

- when the atom with the lone pair doesn't have a negative charge, it will incur a positive charge, while the atom receiving the lone pair will incur a negative charge

## ② An allylic positive charge

- only one curved arrow required

- arrow goes from the  $\pi$  bond to form a new  $\pi$  bond

- conjugated  $\pi$  bonds are separated from each other by exactly one  $\sigma$  bond

- Never place the tail of a curved arrow on a positive charge!!!

## ③ A lone pair adjacent to a positive charge

- only one curved arrow required

- the tail of the arrow is placed on the lone pair, and the head is placed to form a  $\pi$  bond between the lone pair and the positive charge

- remember: conservation of charge!



#### ④ A $\pi$ bond between 2 atoms of differing electronegativity

- Electronegativity = the ability of an atom to attract electrons
- move the  $\pi$  bond up onto the electronegative atom to become a lone pair
- a double bond is being separated into a positive and negative charge
  - opposite of the 3rd pattern

#### ⑤ Conjugated $\pi$ bonds enclosed in a ring

- when conjugated  $\pi$  bonds are enclosed in a ring of alternating double and single bonds, we push all of the  $\pi$  bonds over by one position
  - can be clockwise or counterclockwise
- $\pi$  bonds are conjugated when they are separated from each other by one  $\sigma$  bond

\* Rules for determining the significance of resonance structures:

#### ① Minimize charges

- the best kind of structure is one without any charges

- acceptable to have 1 or 2 charges (more should be avoided)

- the resonance structure that will be the major contributor to the overall resonance hybrid will be the one with no charges

- Exception: nitro group ( $\text{NO}_2$ ). It must be drawn with charge separation to avoid violating the octet rule (don't count these charges to take significance into consideration)

② Electronegative atoms such as N, O, and Cl can bear a positive charge, but only if they possess an octet of electrons

- the most significant structure is one in which all atoms achieve an octet

° doesn't matter if an electronegative atom ends up carrying a positive charge (here)

③ Avoid drawing resonance structures in which 2 carbon atoms bear opposite charges

- the structure is insignificant



## \* Delocalized lone pairs

- lone pairs that participate in resonance
- when this is the case, the lone pair occupies a  $p$  orbital rather than a hybridized orbital
  - so that it can overlap with the  $p$  orbitals of the  $\pi$  bond
- this affects the geometry of the molecule

## \* Localized lone pairs

- lone pairs that don't participate in resonance
- the lone pair is not allylic to a  $\pi$  bond
- whenever an atom possesses both a  $\pi$  and a lone pair, they will not both participate in resonance
  - generally, only the  $\pi$  bond ( $p$  orbital) will participate in resonance and not the lone pair
  - lone pair will usually be held on a hybridized orbital (in the same plane as the molecule)

# Bronsted-Lowry Acids + Bases

\* Definition based on the transfer of a proton ( $H^+$ )

- Acid = proton donor
- Base = proton acceptor
- Conjugate Base = what remains of the acid after being deprotonated
- Conjugate Acid = what the base becomes after accepting a proton

\*  $H_2O$  can act both as base and acid:

- when acting acid: conjugate base is  $OH^-$
- when acting base: conjugate acid is  $H_3O^+$

## Flow of Electron Density

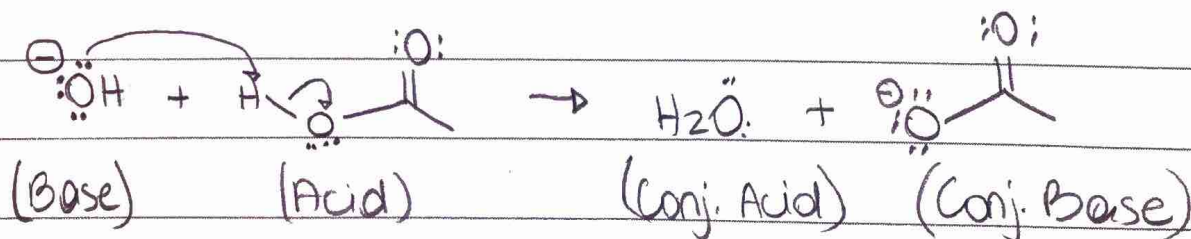
\* There is a flow of  $e^-$  density causing a proton to be transferred from one reagent to another

\* Curved arrows show the reaction mechanism

↳ the mechanism of a  $H^+$  transfer reaction involves electrons from a base deprotonating an acid

↳ acids don't lose  $H^+$  w/out the help of a base

↳ bases need to abstract the proton





↳ the mechanism of proton transfer always involves at least two curved arrows

## Bronsted-Lowry Acidity

### ① Quantitative Perspective

\* Comparing  $pK_a$  values

\* Reaction reaches equilibrium when there is no longer an observable change in the [reactants] and [products].

↳ rate of forward reaction = rate of reverse reaction

\* A strong acid will have a low  $pK_a$  value

\* A weak acid will have a high  $pK_a$  value

\*  $pK_a$  is a measure of acidity

\* If given anions to decide which is a stronger base:

↳ draw conj. acid of each base

↳ compare " "  $pK_a$  values

↳ The stronger acid always generates the weaker base

↳ The weaker acid always generates the stronger base

\* Using  $pK_a$  to predict equilibrium position

↳ Equilibrium always favor formation of the

weaker acid (higher  $pK_a$  value)

## ② Qualitative Perspective

\* To compare acids w/out  $pK_a$ 's, must look at the conjugate bases:

↳ if it is very stable (weak base), the acid is strong

↳ if it is very unstable (strong base), the acid is weak

\* Factors affecting stability of negative charges

### ① Atom

- compare the atoms bearing the negative charge in each conjugate base (always)

↳ For comparing elements in the same row: the most electronegative atom is stronger acid

↳ For comparing atoms in the same column: the biggest (size) atom is the stronger acid

### ② Resonance

- the conjugate base with the most resonance is the stronger acid

- resonance involving (less) more electronegative



atoms is "stronger" than involving (more) less electronegative atoms

- ex: a molecule has delocalized negative charge over 2 oxygen atoms (1) and another has over 1 oxygen and 3 carbons  $\Rightarrow 1 > 2!$

### ③ Induction

- when there is an electronegative atom (usually the halogens) on the molecule, it will withdraw electron density away from the negatively charged region of the structure, stabilizing the negative charge

### ④ Orbitals

- a pair of  $e^-$  in an  $sp$ -hybridized orbital is held closer to the nucleus than a pair of electrons in an  $sp^2$  or  $sp^3$  hybridized orbital

- $e^-$  residing in an  $sp$  orbital are stabilized by being close to the nucleus

- makes a negative charge on an  $sp$ -hybridized carbon more stable than a charge on an  $sp^2$  or  $sp^3$  hybridized carbon

- a  $H^+$  on a triple bond will be more acidic than

a  $H^+$  on a double bond, which in turn will be more acidic than a  $H^+$  on a carbon with all single bonds

### \* ARIO Pattern:

↳ this is the order of importance / rank of the factors affecting stability of negative charges

↳ 1- Atom 2- Resonance 3- Induction 4- Orbital

### Position of Equilibrium and Choice of Reagents

\* The equilibrium represents the competition between two bases for  $H^+$ .

\* Equilibrium will always favor the more stabilized negative charge

\* The position of equilibrium can be predicted by comparing the stability of the base and the conjugate base

### Leveling Effect

\* Bases stronger than hydroxide can't be used when the solvent is  $H_2O$

\* If a base stronger than  $HO^-$  is dissolved with water, the base reacts with water to produce hydroxide

(basically don't even see strong acid)



\* In order to work with bases that are stronger than hydroxide, a solvent other than  $H_2O$  must be employed

\* Ex: an aqueous solution of either  $H_2SO_4$  or  $HCl$  can simply be viewed as an aqueous solution of  $H_3O^+$

\* A more acid molecule has a more stable conjugate base.

\* A less acidic molecule has a less stable conjugate base.

## Solvating Effects

\* Explains differences in stability by considering the interactions between each conjugate base and the surrounding solvent molecules

\* When the ion is bulky ("sterically hindered"), it is less capable of interacting with the solvent

\* When the ion is better solvated, it is more stable

## Counterions

\* Negatively charged bases are always accompanied by positively charged cations

\* Sometimes it is shown, sometimes not

• if it isn't shown it is still there

• it is largely irrelevant, that is why it is omitted

\* Important: ignore the cations when they are indicated and focus on the real players - bases!

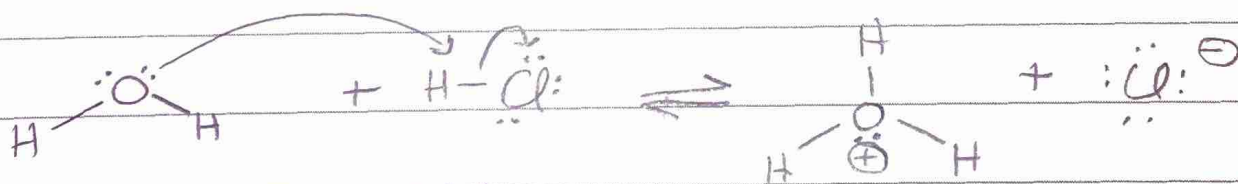
## Lewis Acids and Bases

\* Lewis definition describes acidity and basicity in terms of electrons (rather than protons)

\* Lewis Acid = electron acceptor

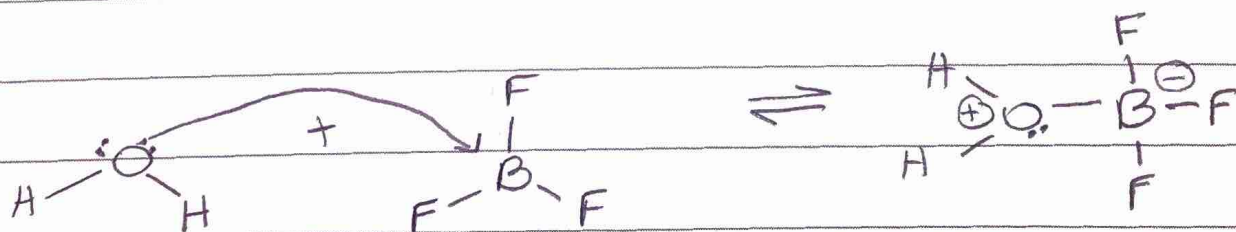
\* Lewis Base = electron donor

\* This is an expanded definition of acids and bases because it includes reagents that would otherwise not be classified as acids or bases



Base (electron donor)

Acid (electron acceptor)



Base (electron donor)

Acid (electron acceptor)



\* Boron and its family have an empty p orbital.

This makes them Lewis Acids

↳ they can accept an electron

↳ they are electrophilic

\* Same is true for carbocations

↳ Nucleophile = donates an electron pair to an electrophile to form a chemical bond.

• All molecules or ions with a free pair of electrons or at least one  $\pi$  bond can act as nucleophiles

• Lewis bases (because they donate electrons)